

Morphology and agglomeration control of LiMnPO_4 micro- and nanocrystals

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Abstract

Microwave-assisted hydrothermal synthesis was used to grow LiMnPO_4 micro- and nanocrystals from acetate precursors. By appropriate adjustment of the precursor concentration and the pH-value of the reactant, the product composition and purity along with the crystal size can be manipulated, resulting in particle-dimensions from around $10\text{ }\mu\text{m}$ down to a few 100 nm . Prisms and plates with hexagonal basal face as well as cuboid and rod-like particles were produced. The effects on the crystal morphology as well as on the materials texture and agglomeration tendency are discussed and a comprehensive agglomeration phase diagram is constructed.

Introduction

The properties of crystalline nanomaterials are intimately connected with their size, shape, and microstructure so that downsizing and tailoring the morphology of materials provides control about,

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e.g., their electronic, magnetic, and optical properties.^{1,2} In addition to the properties of primary particles, their tendency to form aggregates is highly relevant for tailoring desired materials optimized regarding the basic physico-chemical parameters as well as, e.g., their overall toxicity, reactivity, and mechanical stability. Therefore, understanding and controlling accretion of nanocrystals and their oriented or random agglomeration to larger, possibly textured entities is a precondition for adjusting a particular property for the desired application.³ In addition, research activities do not only focus on improving materials for particular applications but include the issue of cost and energy efficient production routes for environmentally benign materials.^{4,5}

A particularly relevant application of nanostructured materials is their usage as electrode materials in electrochemical energy storage devices, where, e.g., Li-diffusion, electronic conductivity, structural stability have to be optimized (see e.g.^{6–8}). In particular, reduction of the ionic and the electronic diffusion lengths and increase of the surface to volume ratio often yields significant improvements in the electrochemical activity. This is particularly illustrated by the olivine phosphates LiMPO_4 with $M=(\text{Mn}, \text{Fe}, \text{Co}, \text{Ni})$ ^{9–12} which can be applied in lithium-ion batteries nano-sized only. The olivine LiMnPO_4 is a promising cathode material owing to the $\text{Mn}^{2+}/\text{Mn}^{3+}$ redox potential at 4.1 V vs. Li and the associated flat discharge curve.¹⁴ Stable reversible capacities of up to 145 mAh/g have already been obtained in carbon-coated nanostructured material consisting of ~ 30 nm thick platelets which extend several 100 nm in the base plane¹⁵ while the performance of rather spherical particles decreases significantly for particle sizes of ~ 200 nm.¹⁶ In addition to the bare size reduction of the particles, the particular morphology is relevant as well, since the ionic diffusivity was predicted not only small but also strongly anisotropic in bulk materials favoring the crystallographic *b*-direction.¹³ Experimental evidence for this anisotropy is indeed deduced from recent studies on nanostructured materials^{15,17} and from single crystals.¹⁸ These results imply that non-spherical crystals with shortest dimensions along the crystallographic direction(s) of high ionic conductivity are optimal for actual applications in lithium-ion batteries. Furthermore, the orientation and the contact of the particles with respect to each other, to the electrolyte, and to the current collector have notable influence on the electrochemical performance of a material.¹⁹

Therefore, the particles surface properties must not only be adjusted to meet the demands of conductivity and chemical stability but also of the particle distribution and agglomeration, which are governed by surface charging effects. In addition to their applicability for energy storage, the olivine phosphates exhibit antiferromagnetic spin order and a large magnetoelectric effect in the magnetically ordered phase which is of fundamental research interest but may yield to future applications, too.²⁰ This is highlighted by the recent discovery of unusual ferrotoroidic domains in LiMPO_4 with $M = \text{Co}$ or Ni which is discussed in terms of future data storage devices.²¹

In this work, we investigate the tailored synthesis of dispersed and agglomerated LiMnPO_4 with dimensions between ~ 100 nm and several μm aiming at fundamental information which enables tailoring nano- and microscaled material. We demonstrate that control of the size and shape of LiMnPO_4 crystals as well as of the particles' tendency to (oriented) agglomeration is possible by applying a fast and low-energy synthesis route, starting from environmentally harmless and non-hazardous precursors. The microwave-assisted hydrothermal method applied here allows controlled synthesis at relatively low temperatures with a non-toxic solvent. Because of their good solubility in water and absence of any additional environmental impact, acetates were selectively chosen as cation-precursors. The phosphate source (di-ammonium hydrogen phosphate) is commonly used as fertilizer in agriculture. Besides ammonia, no further organic additives were used in the educt, thus rendering the chosen synthesis route elementary and reproducible.

Experimental

Applying a hydrothermal synthesis technique, LiMnPO_4 was synthesized using lithium acetate dihydrate, manganese(II) acetate tetrahydrate, and di-ammonium hydrogen phosphate (Aldrich, $\geq 99\%$) solved in deionized water in an off-stoichiometric ratio of 3:1:1 with respect to the ratio of the Li-, Mn-, and PO_4 -ions. The concentration of the Mn-ions in the solution was adjusted to a value between 0.03 and 0.13 mol/l. The pH-value of the reactant was measured with a SevenGo SG2 system (Mettler Toledo) and, starting from a value of 5.5-5.8, adjusted to a value of up to 11.5

by adding diluted ammonia (AppliChem).

10 ml of the solution was put into a 30 ml glass reaction vessel equipped with a magnetic stir bar which was transferred into a Monowave 300 microwave reactor (Anton-Paar) with 2.46 GHz radiation.²² Within a ramping time of 10 min the vessel was heated to a fixed temperature between 160 °C and 220 °C and held at this temperature for 20 min. Subsequent cooling was carried out by the use of compressed air. Note, that high precursor concentrations and superalkaline pH-values could not be achieved simultaneously due to pressure limitations of the device since the vapor pressure of the ammonium adds to that of the other educts. After the synthesis procedure, the precipitate was recovered from the vessel, washed several times with deionized water and ethanol and dried at 90 °C over night.

The energy efficiency of the applied microwave system can be roughly estimated by considering the radiation power for one of the synthesis procedures. The total energy deposit upon heating up the reaction chamber and the educts amounts to about 28 kJ. On the other hand, heating 10 ml of water and the glass reaction vessel (54 g) from 20 °C to 220 °C consumes ≈ 8.4 kJ (+0.3 kJ vaporization heat) and ≈ 7.6 kJ, respectively. Neglecting any effects due to the chemical reaction hence implies that the efficiency of this laboratory system is roughly about 50%. Note, that this value may easily be increased when up-scaling and optimizing the process so that the method offers very high efficiency compared to any ceramic or conventional hydrothermal procedures.

X-Ray powder diffraction (XRD) was performed in Bragg-Brentano geometry (Siemens D500) applying Cu-K $_{\alpha 1}$ and Cu-K $_{\alpha 2}$ radiation ($\lambda_{1/2} = 1.54056/1.54433$ Å). The measurements were taken in the 2θ range from 10° to 70° with a step size of 0.02° and integration time of 1 s (short) or 10 s (long) per step. Prior to the measurements, the powders were dispersed in isopropyl alcohol and dripped on a glass sample carrier. Structural phase analysis was conducted with the FullProf Suite 2.0 program.²³ The morphology of the material was studied by means of a ZEISS Leo 1530 scanning electron microscope with an acceleration voltage of 9 kV. Preliminarily, the samples were coated with a thin gold layer of about 10 nm with a Balzers Union SCD 004 sputtering device under Argon atmosphere.

Results and discussion

Synthesis parameters

Solutions of the individual precursors are pellucid and show a pH-value of 8.1 ((CH₃COO)Li), 7.5 ((CH₃COO)₂Mn) and 8.1 ((NH₄)₂HPO₄), which is a result of the soft basic properties of CH₃COO⁻ and HPO₄²⁻ ions. A white precipitate is formed upon mixing of dissolved (NH₄)₂HPO₄ and (CH₃COO)₂Mn, which is accompanied by a drop of pH-value to 5.5. The addition of (CH₃COO)Li has little effect. No color change can be observed upon alkalizing the solution with ammonia up to a pH of around 10.7. Above this value the color changes to beige and eventually brown, possibly because of the oxidation of Mn²⁺ to manganite or manganese dioxide with air oxygen.

In order to investigate the white precipitate, solutions with pH of 5.5 (starting solution), 9 and 11 were dried and the products were measured by means of XRD (see the supporting information). All three samples exhibit the diffraction pattern typical for NH₄MnPO₄·H₂O.²⁴ However, the XRD patterns of the samples prepared at pH 5.5 and 11 show a high background, which points to the presence of amorphous phases. The sample prepared at pH 9 exhibits sharp peaks and a low background which is characteristic for a good crystallinity. All samples show a high degree of particle orientation in the (010) plane which is most pronounced in the sample prepared at pH 9. This predominant alignment can be explained by the plate-like morphology of the obtained crystallites (for electron micrographs see the supporting information).

The subsequent hydrothermal syntheses as described above yield white to beige colored powders. The pH of the reaction products as recovered from the microwave reactor undermatched the pH of the solutions before reaction by an average value of 1. All washed and dried materials were studied by powder XRD and characteristic patterns of the olivine Pnma structure realized in LiMnPO₄ were found (see the supporting information). A rough inspection of the data shows that several samples exhibit Li₃PO₄ and Mn₂(OH)PO₄ phases in addition to the main phase. Hence, a continuative phase analysis was made for each sample by executing a basic multi-component phase refinement of the XRD patterns by fitting the mass fractions of the three compounds LiMnPO₄

(ICSD #97763²⁵), Li_3PO_4 (ICSD #25816²⁶), and $\text{Mn}_2(\text{OH})\text{PO}_4$ (ICSD #16928²⁷) with pseudo-Voigt profile functions. The results of this analysis for materials synthesized with a fixed precursor concentration of 0.03 mol/l with respect to the Mn^{2+} -ions in the starting solution are shown in Fig. 1 for various pH-values of the reactant and synthesis temperatures.

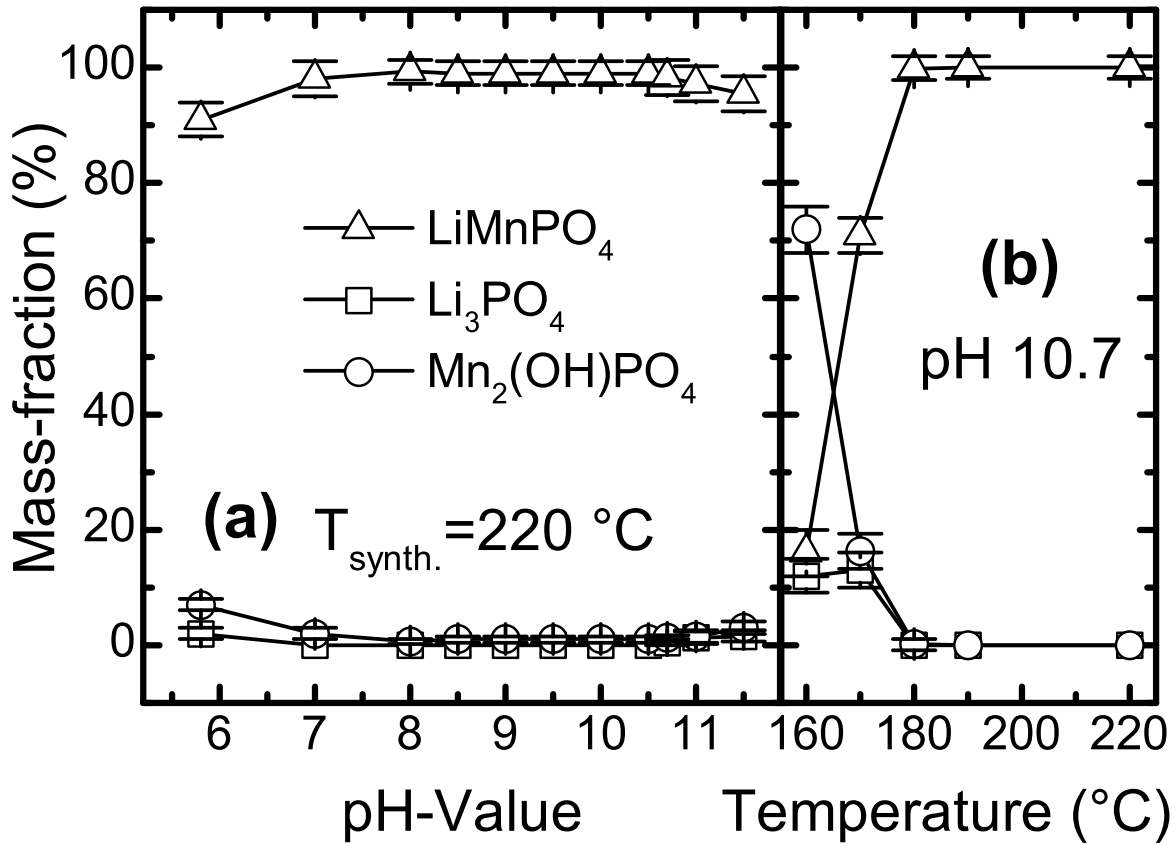


Figure 1: (a) Weight fraction of LiMnPO_4 , Li_3PO_4 and $\text{Mn}_2(\text{OH})\text{PO}_4$ in dependence of (a) the educt pH-value at fixed temperature and (b) the synthesis temperature at fixed pH-value as deduced from Rietveld fits to the XRD data.

The data in Fig. 1 (a) show that, at the synthesis temperature of 220°C , the production of phase pure LiMnPO_4 without formation of side products is possible in a wide pH-range between 7 and 10.7. Below and above this regime the materials exhibit Li_3PO_4 and $\text{Mn}_2(\text{OH})\text{PO}_4$ impurity phases in the %-range which can be detected by the XRD experiment. Note, that most of the overview XRD patterns were measured with a short integration time so that the error bars are in the range of a few mass-percent. The XRD patterns discussed in the next sections were measured

more accurately.

The regime of stable LiMnPO_4 production coincides with the pH-range favoring crystalline $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$ without amorphous side products. This compound is known to be a precipitate precursor at the synthesis of LiMnPO_4 due to its structural similarities.^{28,29} We thus assume that $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$ is a necessary precursor for the synthesis of LiMnPO_4 under these conditions. The residual amorphous phases present in the educt are likely to be reacted to the impurity phases Li_3PO_4 and $\text{Mn}_2(\text{OH})\text{PO}_4$. Note, that calculations in Ref.³⁰ suggest that a production of Li_3PO_4 is more likely at superalkaline conditions which favor the phosphate form PO_4^{3-} in aqueous solutions. This conclusion is supported by the results at hand.

In Fig. 1 (b), the effect of synthesis temperature variation is illustrated for fixed pH = 10.7. The data show that, under these conditions, phase pure synthesis of LiMnPO_4 occurs at synthesis temperatures exceeding 180 °C. In general the results in Fig. 1 demonstrate that with the chosen precursors the experiment offers a wide range of parameters where LiMnPO_4 can be successfully synthesized while their variation may be used to control the morphology and the size of the produced particles. In the following, the synthesis temperature was chosen to be 220 °C in all cases.

Particle size and morphology

Fig. 2 gives an exemplary overview on the LiMnPO_4 morphologies accessible by the applied synthesis route. The presented electron micrographs are grouped according to the three different precursor concentrations (**L**: 0.03 mol/l Mn^{2+} -ions; **M**: 0.075 mol/l Mn^{2+} -ions; **H**: 0.13 mol/l Mn^{2+} -ions) which were used. Within each group, the images are arranged with respect to the pH-value of the reactant before the synthesis.

The largest LiMnPO_4 crystals are obtained at a low precursor concentration and neutral to alkaline pH-values. Sample L1 consists of hexagonal prisms with a base-length of about 10 μm and a height of 3 to 5 μm . As demonstrated by the following images, the hexagonal basal face is a typical element of hydrothermally synthesized LiMnPO_4 particles (cf. also Ref.³¹). Increasing the pH-value to 9 (sample L2) affects both the crystal size and the agglomerative behaviour of

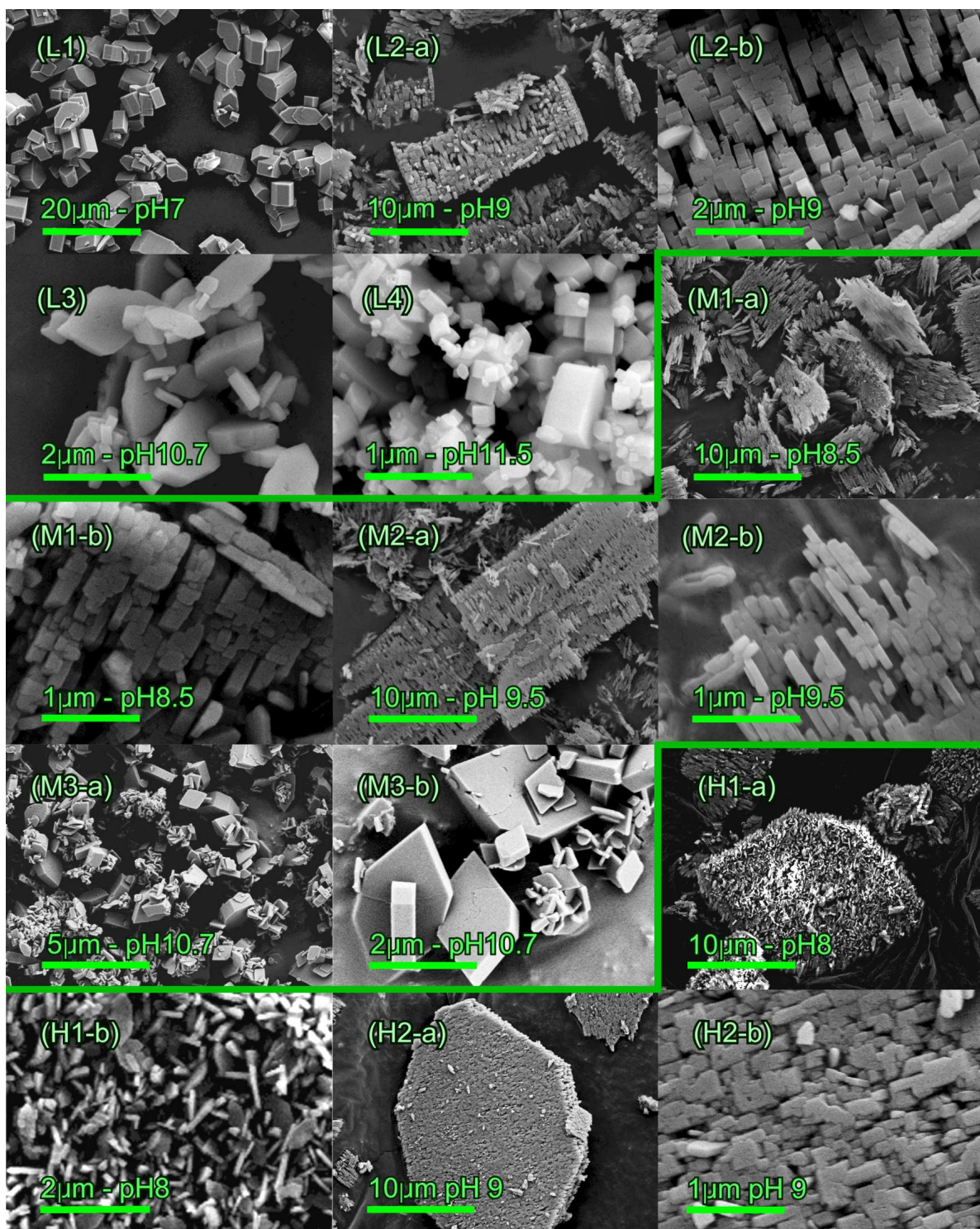


Figure 2: Electron micrographs of LiMnPO_4 samples, synthesized with three different precursor concentrations and various pH-values (see the text). **L**: 0.03 mol/l Mn^{2+} -ions; **M**: 0.075 mol/l Mn^{2+} -ions; **H**: 0.13 mol/l Mn^{2+} -ions.

the particles. The material features rectangular aggregates with an ordered texture and consisting of sub- μm -sized cuboidal particles. This strong tendency to aggregation disappears when the reactant is heated at even more alkaline conditions. Sample L3 produced at pH 10.7 contains arbitrarily arranged platelets, again with a hexagonal however rounded basal face. The longest edge amounts 1 – 2 μm and the platelets heights are sub- μm . The smallest particles obtained at this precursor concentration were produced at pH of 11.5 which is the highest pH-value applied. While the morphology of the resulting particles is similar to sample L1, the crystals are sub- μm to nano-sized in any direction. Note, however, that at this strong alkaline conditions no phase pure LiMnPO_4 synthesis was possible (see Fig. 1).

The above described tendency to agglomeration into ordered textures intensifies when increasing the precursor concentration. At pH-value of 8.5 (sample M1) the process yields plates with dimensions of about 10 μm consisting of cuboidal particles with a typical size of some 100 nm. A similar hierarchically assembled structure is realized in sample M2, synthesized at pH 9.5. When increasing the pH-value, the size of the agglomerated structures extends. Concomitantly, growth of the individual particles seems to favour a particular direction which yields rod-like crystals with a typical length of about 0.5 μm being the elements of the agglomerates (see images M2-a and M2-b). Further raise of alkalinity to pH = 10.7 (sample M3) stops the strong aggregative tendency. Sections M3-a and M3-b of Fig. 2 display well-developed hexagonal platelets, however with a very broad size distribution with in-plane particle dimensions from about 2 μm down to some 100 nm.

At the highest precursor concentration of 0.13 mol/l Mn^{2+} -ions, textured agglomerates are observed in the whole accessible pH-range. All materials exhibit well-ordered agglomerates with hexagonal to octagonal shape and sizes larger than 10 μm . The electron micrographs of sample H1, synthesized at an educt pH-value of 8, indicates that the aggregates consist of non- or low-ordered sub- μm particles. Note, that the structure analysis described below reveals that the crystallites exhibit an ordered texture, thus rendering the apparent disorder surface related. This is more clearly visible in the micrographs H2-a and b of the material produced at pH 9. Here, the ordered texture of the agglomerates surface formed by cuboidal particles with a typical size of some 100 nm is well

visible. Interestingly, the flake-like aggregates can be multilayered, thereby forming 'agglomerates of agglomerates'. Note, that neither the morphology of the primary particles nor of the aggregates changes when the educt pH is increased 10.4 (not shown).

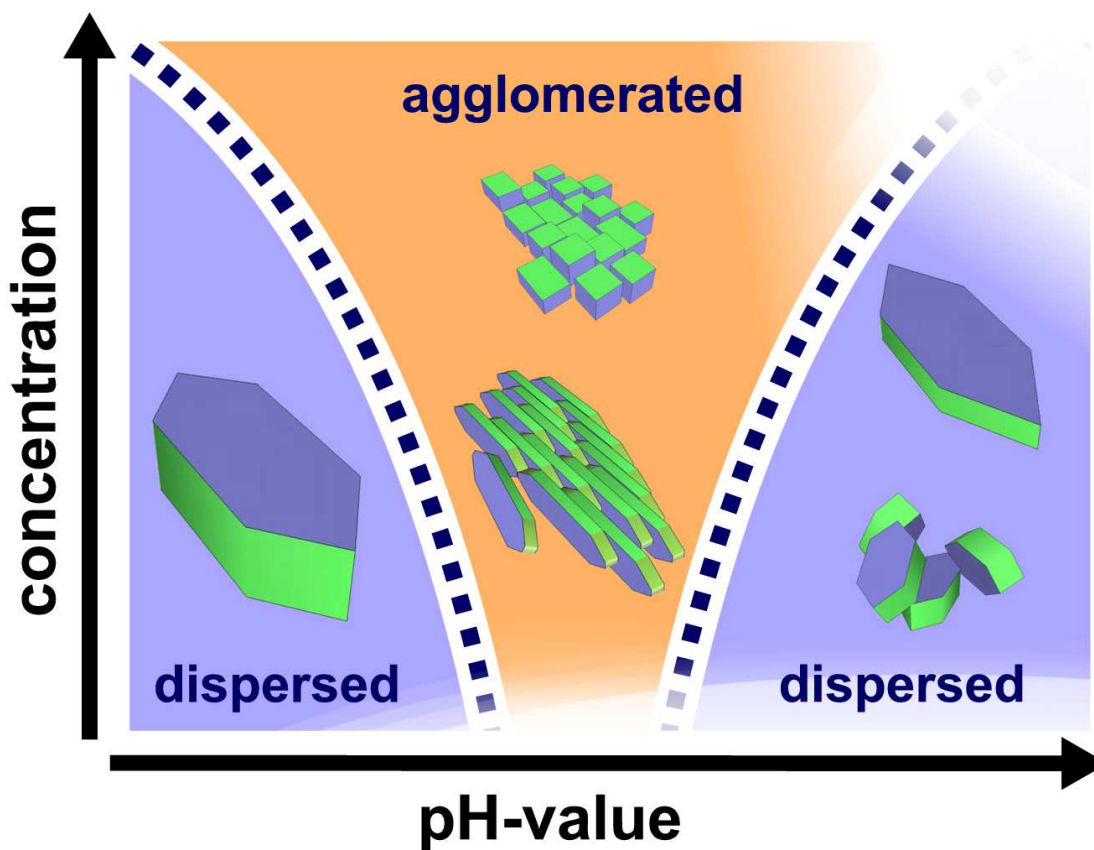


Figure 3: Schematic sketch of the pH-value and precursor concentration dependence of particle-size and -agglomeration. The regime of stable dispersion is stained blue, the regime of ordered agglomeration is stained orange.

Summarizing, variation of the precursor concentration and the pH-value of the reactant strongly affects the size and shape of the individual crystallites and of the agglomerates. Note, that the particles morphologies obtained after hydrothermal conditions are not related to the morphology of the crystalline $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$ precursor which was recovered from the starting solution by conventional drying.

The results are illustrated schematically in Fig. 3. In general, the particle size decreases upon raising alkalinity of the reactant and increasing the precursor concentration. The latter yields an

increase of the number of condensation nuclei which explains the smaller particle sizes. This behaviour is however modified by simultaneous variation of the particles tendency to agglomerate into larger entities, which also depends both on the pH-values of the solutions and the precursor concentrations. Agglomeration is usually favoured by attractive van der Waals interactions and prohibited by the electrostatic surface potential. In Fig. 3, the region of textured agglomerates is indicated by orange colour. In contrast, blue colour signals the parameter space where individual particle formation is favoured.

At highest pH, the particles are medium-sized and show low tendency to clot to large structures. Presumably, the strong alkalinity of the solution causes a finite negative surface electrostatic potential preventing contacts of the relatively low concentrated seeds and particles. Straightforwardly, both increasing the precursor concentration and decreasing pH stabilizes the coagulation processes which is visible in Fig. 3. In case of neutral surfaces which in the case at hand seems to be realized between pH 8 and 9.5, agglomeration should occur regardless of the educt concentration (see, e.g., Ref.^{32,33}) which is indeed observed in the experiment. Further acidising is supposed to generate positively surface charged and hence well dispersed particles. In addition to appropriate charge stabilization in water a narrow primary particle size distribution is necessary for the formation of ordered agglomerates, too.³⁴ Indeed, the supporting effect of adapted primary particle size and shape is evident if the strong agglomeration regime in Fig. 2 is compared to the region of dispersed particles.

Note, that very recently the isoelectric point in LiFePO_4 was found at $\text{pH} = 4.3$.³⁵ Firstly, the apparent deviation from pH between 8 and 9.5 which is observed in our experiments for LiMnPO_4 needs to be qualified by a small uncertainty of the pH determination during particle formation. After the syntheses, the pH-values were slightly lower (by a maximum of 1) as compared to the educts which is due to the release of NH_4^+ -ions from the $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$ precipitate. Acidic conditions however were never reached in our experiments so that there is a clear contrast to LiFePO_4 . In iron phosphate, acidic groups resulting from unsaturated metallic cations are supposed to dominate the surface properties in aqueous solution leading to a negative surface charge for pH-

values even below 3.³⁶ This coincides with the isoelectric point at acidic pH-values. In contrast, our data presented above show that the dominant surface groups of LiMnPO_4 are less acidic. We suggest that a lower attraction of OH^- -ions in LiMnPO_4 as compared to LiFePO_4 causes the shift of the isoelectric point to the basic regime which is consistent with lower acidity of aqueous Mn^{2+} -ion as compared to Fe^{2+} ($\text{pK}_a(\text{Mn}^{2+}) = 10.59$, $\text{pK}_a(\text{Fe}^{2+}) = 9.5$).

Structure analysis and preferred orientation effects

A more detailed structural analysis was conducted for two samples (M2, M3) synthesized at a moderate precursor concentration of 0.075 mol/l and at pH-values of 9.5 and 10.7, respectively, representing the two different cases of highly agglomerated and dispersed particles. Fig. 4 shows the measured XRD patterns of both samples along with the calculated pattern (with pseudo-Voigt profile functions) according to Ref.,²⁵ including the March-Dollase Model, and the resulting residual. Both patterns exhibit the diffraction peaks characteristic for the orthorhombic Pnma structure, however huge differences in the relative peak intensities between both samples are visible. While sample M3 shows the pattern of arbitrarily oriented particles expected for dispersed particles, especially the (200), (210), (301), (410), and (610) peaks at $2\theta = 17.0^\circ$, 22.4° , 31.8° , 37.5° , and 54.9° are enlarged in sample M2 as compared to Ref.²⁵ This effect is well known for oriented powders and the aberration can be modeled by applying the March-Dollase Model³⁷ for a preferred powder orientation, with the March-Dollase function:

$$P(r, \alpha) = (r^2 \cos^2(\alpha) + r^{-1} \sin^2(\alpha))^{-3/2}. \quad (1)$$

$P(r, \alpha)$ describes the volume fraction of the material oriented at an angle α with respect to the \hat{n} -axis, which is normal to a specific crystallographic plane (hkl), and a parameter r . Refinement of r in the accordingly modified pattern with the (200), (210), and (301) reflection yields the coefficients listed in table 1. Considering the (hkl)-planes (410) and (610) does not further improve the agreement between model and measured data. Note, that only the orientation, not the structure

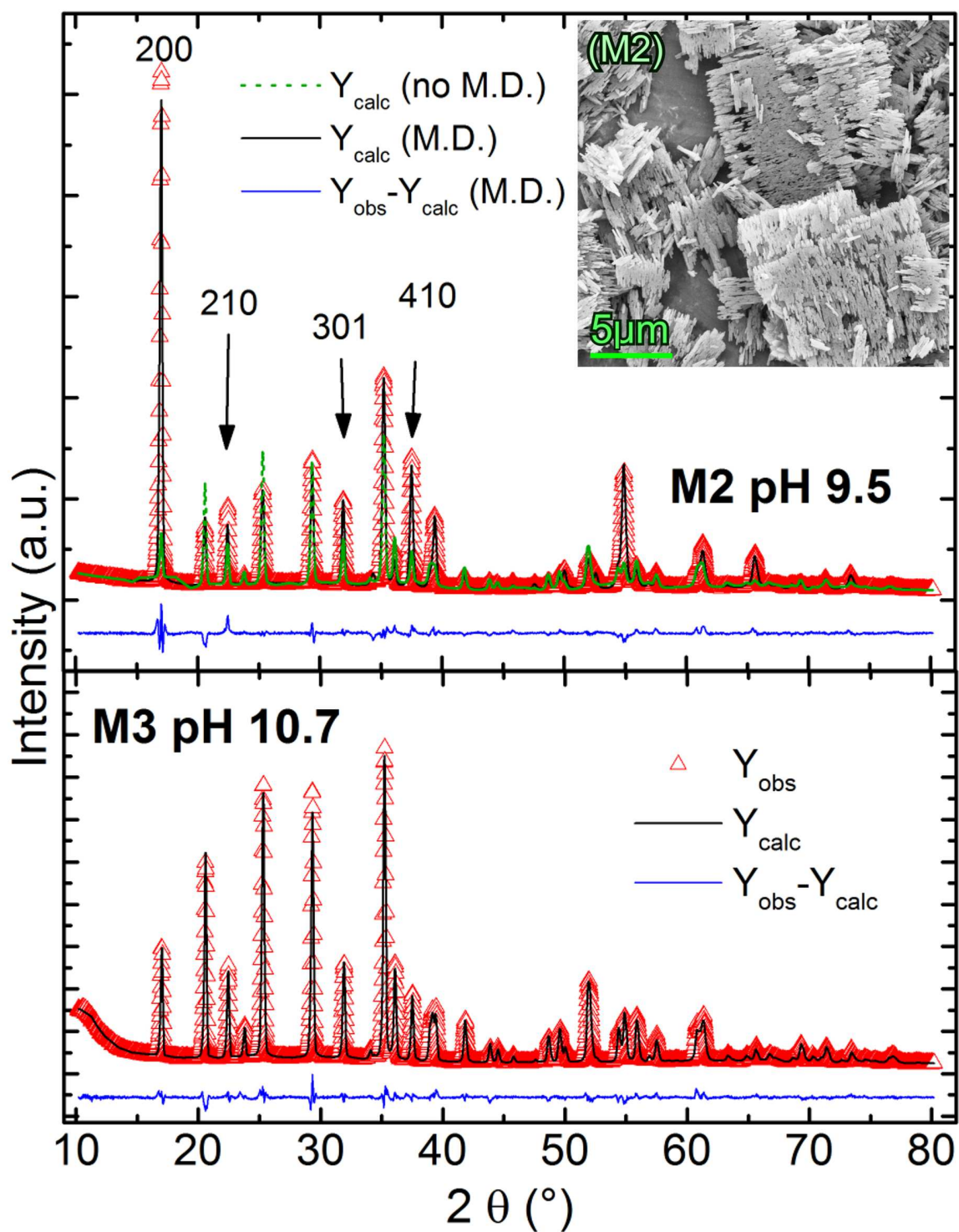


Figure 4: Measured and calculated XRD patterns for sample M2 and M3. The labeled peaks for M2 are enlarged as compared to the calculated pattern (green line). This effect is considered by means of the March-Dollase model (black line). Inset: SEM picture of sample carrier after wet preparation process.

was refined.

Table 1: Calculated March-Dollase multi-axial model parameters for sample M2.

Pref. (hkl)	\hat{n}-fraction	r
(200)	0.936	0.503
(210)	0.054	0.441
(301)	0.009	0.308

The obtained parameters show that the primary crystals are mainly aligned in the (100) plane. This corresponds to the orientation of the crystallographic bc -plane perpendicular to the plane generated by the X-ray beam and thus parallel to the sample holder. This outcome might be caused by the interplay of two effects, i.e. (1) an anisotropic tendency to agglomeration of the primary nanocrystals, and (2) the arrangement of the plate-like aggregates of sample M2 parallel to the sample carrier (see the inset of Fig. 4). The latter might result from the wet preparation process. In this way, the alignment of the primary particles leads to the fixing of one preferred axis (see Fig. 5). The specific orientation of the crystallographic b - and c -directions can not be deduced from these data. A comparison with electron diffraction data from Ref.³¹ however suggests that the direction of longest particle dimension corresponds to the c -axis.

The results imply anisotropic agglomeration tendencies between the bc -surfaces (no or very low tendency to agglomeration) and the ab - and ac -surfaces, respectively (strong agglomeration), and hence indicate different tendencies to charge accretion and thus different repulsive forces. To be specific, the results imply higher charging of the bc -surface even in the regime of high agglomeration as compared to the other surfaces.

From a structural point of view, the bc -planes are formed by layers of corner-sharing MnO_6 octahedra separated by layers containing the PO_4 tetrahedra and Li-channels. Whereas, in the ab - and ac -planes only layers containing different polyhedra can be found (for illustration see for example²⁸). The higher charging of the bc -surface might hence result from the presence of just one species at the surface and thus the accretion of only ions with the same sign of charge, e.g., Mn-hydroxocomplexes formed by unsaturated ions in the Mn-oxide layer (acidic behavior) or the formation of hydrogen phosphate with PO_4^{3-} groups (basic behavior).

The observed powder XRD orientation effect can be seen to some extent in the patterns of all materials which exhibit the tendency to form ordered agglomerates. In this respect, the analysis of the XRD data confirms the general trends in agglomeration summarized in Fig. 3.

Diverse surface functionalities were artificially applied by Xia et al.³⁸ to Ag-nanocubes dispersed in water. Their observation of self-assembled structures confirms a significant influence of the surface properties on the growth, the texture, and the final size of the agglomerates. Similarly, as outlined above we propose that the formation of diversely shaped and partly oriented agglomerates found in LiMnPO_4 nanostructures is governed by the particular surface properties. Note, that a different mechanism is proposed for LiFePO_4 microstructures which have been recently synthesized via a hydrothermal route.³⁹ While similar to our findings self-assembled and ordered agglomerates of LiFePO_4 nanocrystallites are observed, Su *et al.* emphasize the relevance of the reaction time and of the template properties of the precursors for the particular morphology of the aggregates while the specific effect of surface charge is not taken into consideration.

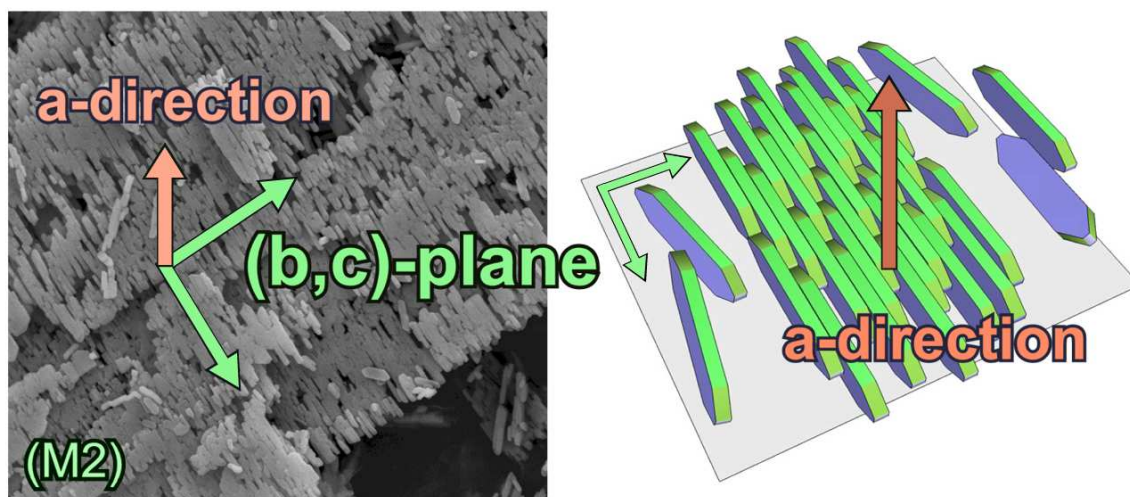


Figure 5: Relation between agglomeration behaviour of primary particles and crystallographic directions. The (b,c) -surface is green coloured, all perpendicular surfaces are blue coloured.

Summary

We have demonstrated the influence of the fundamental synthesis parameters pH-value and precursor concentration in the energy efficient microwave-assisted hydrothermal synthesis process of LiMnPO_4 . Upon variation of these parameters, we observe regimes where the product consists of well-dispersed particles shaped as hexagonal prisms which size is adjustable from several μm down to the sub- μm range. In addition, we found a region of parameter space where the particles exhibit a strong agglomerative behaviour, thus forming plate-like aggregates. The analysis of the XRD patterns reveals preferred orientation of the particles and an anisotropic tendency to agglomeration, favouring oriented aggregation in the (b,c) -plane. These results used to construct the agglomeration phase diagram which is discussed with respect to the particles surface charging behaviour. In summary, appropriate choice of the pH-value and the precursor concentration enables tailoring the size and morphology of LiMnPO_4 micro- and nanostructure as well as controlling the dispersion or agglomeration.

Acknowledgement

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Supporting Information Available

Powder XRD patterns of all samples discussed and SEM images of the recovered precipitates are presented in the supporting information.

This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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